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APPLICATION OF SPECTROSCOPIC RESEARCH METHODS FOR MOTOR OIL CONDITION AND QUALITY EVALUATION

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Abstract

The study presents an application of spectroscopic methods to diagnose motor oil condition and quality basing on FT-IR and ICP methods.

Keywords: *FT-IR spectral analysis in infrared radiation, FT-IR spectrometry, ICP plasma emission atomic spectrometry*

1. Introduction

In order to determine motor oil condition there are used different research methods. Research laboratories run effective projects of oil analysis which include motor oil condition monitoring in order to determine efficiency and remaining period of oil lifetime basing on its degradation and pollution. Tests of physical properties performed in typical analysis laboratory of used oils (frequently used are modified procedures of ASTM (American Standard Test Method) containing analysis of: viscosity, TBN (alkalinity), TAN (acidity), water content (Karl Fisher), solution with fuel and insoluble compounds analysis [2,4,6,7,9]. The parameters mentioned are essential information about oil condition itself but also about the technical condition of the motor in which it was used.

Spectroscopic methods [5,6]are increasingly frequently used in research laboratories for motor oil condition monitoring.

Spectroscopy is a science dealing with theoretical and practical relations between matter and electromagnetic radiation. Such methods include: spectral analysis in infrared radiation (FT-IR) and ICP element para - plasme analysis. The first one is used mostly to monitor the motor oil condition via its physical and chemical feature evaluation. The latter one belongs to methods of motor oil evaluation via observation of trace amounts of particles created from motor or other device element wearing transported by oil. Basing on performed examination results one can conclude about motor technical condition and about necessity of oil change.

The article introduces application of selected spectroscopic methods in recently performed researches [5] led in order to analyze and evaluate of motor oil condition. Methods presented in this publication refer to research of selected motor oils used in lorry cars. The oils in discussion were also examined by traditional methods, but their deeper discussion was not included in this article. The examined motor oil samples of particular mileage were taken and changes occurring in them were analyzed.

2. Spectral analysis in infrared radiation (FT-IR)

IR spectrophotometer is a method based on infrared radiation absorption by oscillation particles [5,8,10,11]. New measurement possibility was created by introducing IR spectrometry with Fourier transformation. Infrared radiation covers electromagnetic spectrum range between visual and microwave radiation. The biggest practical value has a wave band of 4000 cm^{-1} - 400 cm^{-1}[8,10,11]. IR spectrum of the examined oil sample is presented as a diagram picturing relative radiation intensity coming through the researched oil (transmittance) in relation to recorded spectral band ($E \infty \nu$ [cm^{-1}]) and it is characteristic feature of particular chemical compound, thus it is used to identification of compounds.

Oscillating spectra of particles are examined with classical infrared spectrometers as well as spectrophotometers with Fourier transformations [5,8].

An example of application of FT-IR transmission technology are results presented in research work [5] performed within wave range of 4000- 450 cm^{-1}. The spectra of examined oil during exploitation were compared with the reference spectrum of fresh oil. During interpretation of selected spectra there were observed quality changes which mostly picture the lack of absorption bands of additives and increase of bands characteristic for oxidation products (Fig.1).

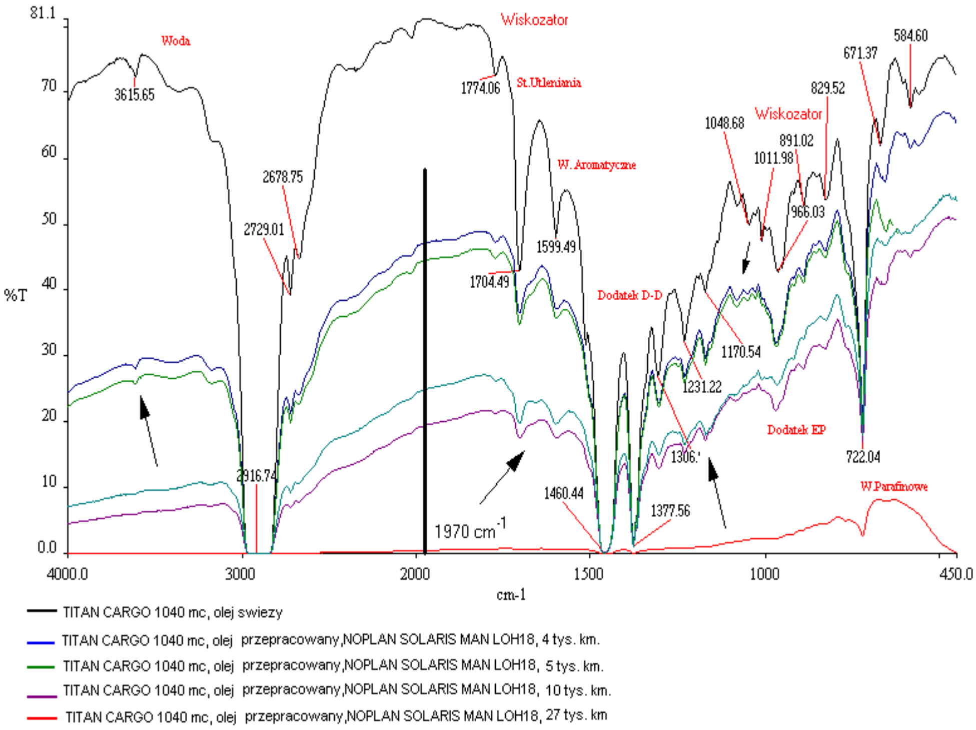

Fig.1. Example of spectrum for fresh and overworked oil TITAN CARGO MC [5] MC (wiskozator - viscosator; stopień utleniania - oxidation rate; w. aromatyczne - aromatic hydrocarbons; w. parafinowe - paraffin hydrocarbons; dodatek -additive; świeży olej - fresh oil; olej przepracowany - overworked oil)

Essential in this case for interpretation are bands: 3640 cm^{-1},1600 cm^{-1}. In relation to these bands we can read from the spectrum that decrease (flattening) indicates the following data about quality content of oil – antioxidant additive is decreasing (peak 3640 cm^{-1}), amount of aromatic hydrocarbons is decreasing (peak 1600 cm^{-1}). The distinct widening and more circular shape of peak 1600 cm^{-1} gives signal that oxidation and nintriding processes go on.

Information about quality composition changes in motor oil is not the only information possible to conclude from spectra. Beside oil content evaluation we can also read certain properties of motor oil. For instance decrease in two previously discussed absorption bands shows increase in oil viscosity (Fig.2.). Knowing that you can omit kinematic viscosity analysis. High depletion of D-D additive (peak 1230 cm^{-1}) and drastic drop of EP and AW (anti-wear) additives (peak 970 cm^{-1}) can suggest already without additional TBN analysis, that TBN drops.

This example shows the reading out of TBN and kinematic viscosity increase without performing costly and time consuming traditional analyses. Disappearance of peaks 1000-1100 cm^{-1} suggests the presence of glycol in motor oil.

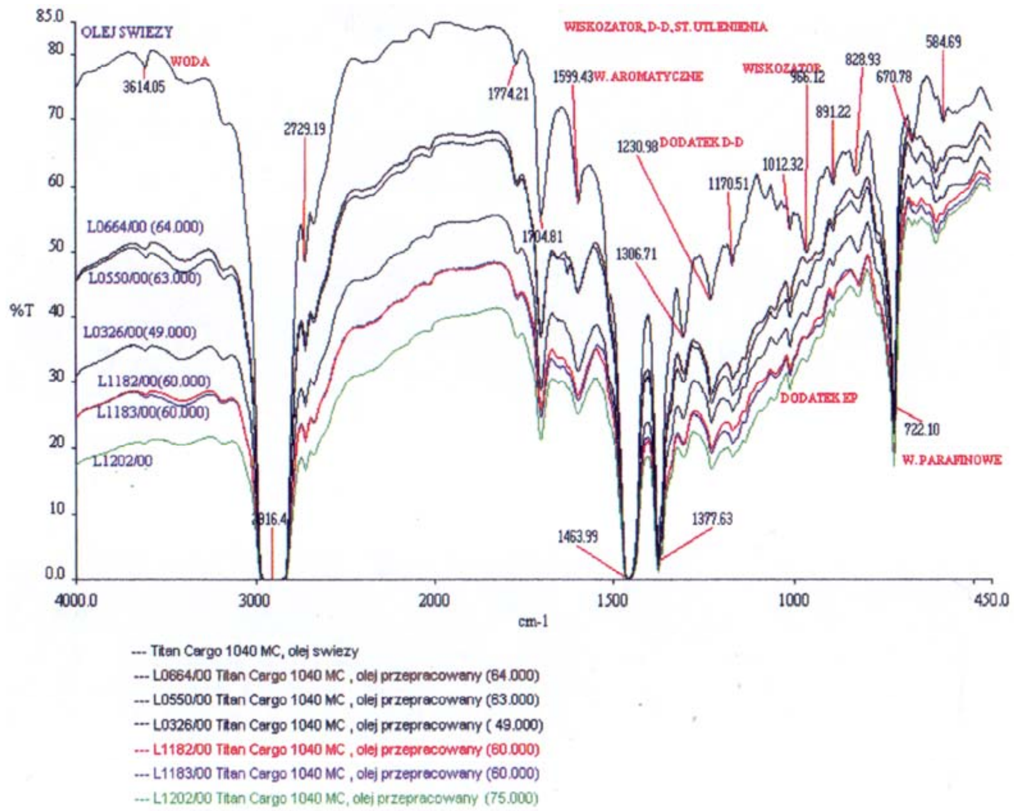

Fig.2. Example of spectrum for fresh and overworked oil TITAN CARGO MC [5] MC (wiskozator - viscosator; stopień utleniania - oxidation rate; w. aromatyczne - aromatic hydrocarbons; w. parafinowe - paraffin hydrocarbons; dodatek -additive; świeży olej - fresh oil; olej przepracowany - overworked oil)

Fig.1 and 2 presented above indicate clearly changes occurring in oil during exploitation. There are three areas which can be defined in which clear differences happen when comparing to fresh oil. Besides sooner mentioned possible interpretations of spectra, IR spectroscopic technology is a complementary analysis allowing also:

- base oil identification (mineral, PAO, ester oil)
- definition of oil compatibility, choice of complements,
- definition of enrichment additives and their share in fresh oil
- detection of processes (i.e. oxidation, nitridation, sulfating)
- detection of additives and pollutions (water, fuel, mineral substance etc.)

3. Element anlysis by ICP (Inductively Coupled Plasma)

ICP method is used for automatic marking of oil chemical content in argon plasma [5]. It is used for analysis of particles 5 μm.

Inductively excited plasma consists of atoms and ions of argon and proper amount of electrons and it is visible as intensively shining discharge of characteristic shape. A sample in form of solution or suspension is transformed into spray by atomizer. Elements excited in plasma emit radiation of different wave lengths – it is polychromatic emission. Polychromatic radiation is then dispersed according to wave length so it is possible to identify particular excited atoms or ions and to measure radiation intensity. An example of application of this spectroscopic method for motor oil condition is research work [5], in which research was done according to research standard: ASTM D 4951 – 92 (fresh oil), ASTM D 5185 – 93 (overworked oil).

The ASTM D4951-92 method determines a way of content marking for elements coming from enrichment additives in motor oils while the second standard determines a way of marking of element content from metals coming from wearing of cooperating parts and impurities in overworked oils.

ICP spectral element analysis – enables marking of the following element groups:
- elements originating from oil (additives): Zn, P, B, Ca, Ba, Mg, Na,
- elements originating from friction wear of motor parts: Fe, Cr, Ni, Mn, Cu, Pb, Al, Mo,
- elements originating from impurities and additives: (Si : Al = 1,5:1), Ca, Na, B.

Equipped with such technique we can quickly determine with high precision whole standard set of elements. The full range of element analysis by ICP method for monitoring purpose should cover the following elements:

- Fe, Pb, Cu, Sn, Si, Al, Sn, Ag, Na, B, Li, Cr, Ni, Mo, Mn, V, Sb, W, Ti, Cd – usually measured within range 0 – 100 mg/kg (ppm),
- Zn, Ca, Mg, P, Ba – measured within range 0 – 900 mg/kg (ppm),
- S – measured within range 0 -10000 mg/kg (ppm).

Essential feature of ICP-AES is possibility of simultaneous marking of element group and it is most often used to marking of metal content in fresh and overworked lubricating oils.

Using research results from [5] the below presented examples (Table 1,2) show element analysis of motor oil performed by ICP method.

Tab 1. Example of element analysis of TITAN CARGO MC motor oil [5]

1	Sample number	Acceptable values	L 0617
2	External look		yellow
3	Sampling date	ASTM D 5185-93	---------
4	Mileage		52000 km

5	Element content; [ppm]		
	B	15-25 ppm	21.3
	Ca	-----	221.5
	P	additive	1112.0
	Zn	-----	328.0
	Pb	10-20 ppm	56.2
	Fe	100-150 ppm	22.0
	Mg	10-30 ppm	79.2
	Mo	6-10 ppm	71.7
	Cr	5-10 ppm	31.9
	Sn	10-20 ppm	48.9
	Si	30-45 ppm	1.1
	Al	15-30 ppm	3.2
	Cu	25-40 ppm	7.9
	Ni	4-8 ppm	3.9
	Na	5-10 ppm	0.5

Tab 2. Results of oil element analysis with ICP method [5]

No	**Examined parameter**		**Marking value**			
1	Sample number		Fresh oil	L0730	L1062	L1285
2	Sample origin		Fresh oil	Opel Omega	Opel Omega	Opel Omega
3	Mileage		-----	**13500 km**	**27000 km**	**47000 km**
4	Element content [ppm]	ASTM D5185-93				
	B		<0.1	10	28	<0.1
	Ca		3680	3472	3650	3600
	P		480	339	252	275
	Zn		1	106	98	82
	Pb		3	13	18	18
	Fe		2	24	43	56
	Mg		8	47	45	40
	Mo		<0,1	7	6	9
	Cr		<0,1	1	1	2
	Sn		<0,1	3	2	<1
	Si		3	6	6	9
	Al		3	5	8	7
	Cu		<0.1	4	6	9
	Ni		<0.1	4	2	4
	Na		<0.1	<0.1	**<1**	<0.1

The results of oil element analysis, i.e. such elements as lead, magnesium, tin, as well as chromium and molybdenum testify for excessive wear of such motor parts as bearings, sleeves and piston rings. Excessive wear of these parts can result from overheating as a result of overloading and also incorrect motor exploitation within full range of rotational speed (driving habits). Excessive wear of motor parts has direct influence on increased consumption of motor oil.

4. **Basic analytic instruments used in spectroscopic analyses**

In order to perform analysis with spectroscopic technique we use number of analytic instruments provided by tribology laboratories. **FT-IR spectrometers** (for example SPECTRO FT-IR OIL ANALYZER) are designed to used oil analysis [6]. They have dedicated software which detects degradation and pollution parameters from spectrum of a used oil sample. This technique is quick, analysis lasts less than a minute and provides data about oxidation, nitration, sulfating, dustiness, fuel dilution, water and glycol content, and in some cases depletion of additives in used lubrication oils. Because of its speed and trend setting, it became a standard technique in laboratories analyzing large number of used oil tests. **ICP spectrometers** with inductive coupled plasma (for example SPECTRO ARCOS and SPECTRO GENESIS) are recommended when there is need for high analysis accuracy, e.g. additive analysis in oil enrichment factories. These basic instruments can be complemented with other analytical instruments. Ferrography enables magnetic separation of particles in oil sample arising from motor wear and ordering them in relation to their size on microscope base.

More and more frequently automatic particle analysis technique is used. LASERNET FINES particie analyzer enables measurement of particle quantity contained in oil, determining their shape, origin, size, recording data and determining a trend. It simultaneously counts particles (particle counter) and determines dust pollution rate of oil. It is a tool simple in usage and can be also equipped with sample feeder what makes it an ideal instrument for laboratories analyzing large number of samples [6].

However, for objective determination of oil condition it is necessary to examine parallels such features as: acidity (Total Acid Number), alkalinity (Total Base Number), marking of water with Karl Fisher method. They are most often performed tests ASTM (American Standard Test Method) for determination of oil degradation and pollution. If more detailed information is needed than obtained from FT-IR spectrometer, then often in comprehensive system of oil analyses there is also provided an automatic titrates. ITL Industrial Tribology Laboratory by SPECTRO company fulfils the above requirements for equipment adjustment and compatibility having a comprehensive system for monitoring of machine and motor condition on basis of oil analysis.

5. Final conclusions

The analysis of data from scientific literature and authors' experiments lets formulate the following conclusions:

1. Spectroscopic methods enable quick and efficient analysis and evaluation of motor oil.
2. They are modern methods enabling motor oil examination during motor exploitation.
3. FT-IR spectroscopy enables a comprehensive analysis of composition and change recording which enables differentiation of oil conditions being the basis for usage of this applied methodology of motor oil research.
4. ICP spectroscopy delivers quality and quantity analysis of particles in lubricant oil arisen from wearing of parts. This technique is very effective in detecting defects which are characterized with incorrect increase of metal particles coming from wearing and polluting.
5. At present stage of science and technology it is extremely difficult to precise one universal parameter characterizing in objective way motor oil in any exploitation phase.

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